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# Surface oxygen implanted in titanium by recoil collisions with 1 MeV gold ions

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## Abstract

Oxygen is known to be an important factor in reducing the corrosion rate of titanium, yet small amounts of oxygen on the titanium surface are practically undetectable by standard Rutherford Backscattering Spectrometry (RBS) analysis. The 3.05 MeV nuclear scattering resonance for  $^4\text{He}^+$  on oxygen was used in this study to show that surface oxygen is recoil-implanted by collisions with 1 MeV gold ions and produces a noticeable effect on corrosion test results.

## 1. Introduction

Titanium is a technologically important metal which is used in numerous applications because of its strength and corrosion resistance. The phenomenon of *passivity* is a loss of chemical reactivity occurring for certain materials under certain environmental conditions, and this is one of the most significant characteristics of titanium [1]. Titanium becomes passive, or exhibits passive behavior, because a protective oxygen layer forms on its surface and significantly improves the material's resistance to corrosion in sulfuric acid. Metals which exhibit passive behavior do so only under certain conditions depending upon the metal, the concentration of ions and the pH of the solution in which the metal is immersed, and the electric potential applied to the metal. For example, it has been shown [2] that a sample of titanium undergoing active dissolution in sulfuric acid can passivate simply by adding Ti(IV) ions to the solution.

Cathodic protection has been commonly used for corrosion control since 1824 and anodic protection was introduced in 1954 [3]. Another method of corrosion protection, which involves the addition of an inert or noble metal such as gold or platinum, to the base metal is called *noble-metal alloying*. Ion implantation provides a means for studying the mechanisms of corrosion and the effect of noble-metal alloying on corrosion. Experiments conducted at Oak Ridge National Laboratory [4] show that while being dissolved in sulfuric acid, titanium returns to the passive state if it is implanted with an adequate amount of platinum. Fontana explains [5] that the presence of platinum produces a

galvanic couple which causes the titanium to preferentially dissolve from the surface. The implanted platinum becomes enriched at the surface resulting in spontaneous passivation.

A study similar to these was conducted by Vollmer [6], implanting 1 MeV gold at varying different implant doses. In this case, the corrosion rate of the titanium was monitored using inductively coupled plasma tests and the corrosion state (active or passive) was monitored by open circuit potential measurements [7]. The results showed that the titanium corroded faster (Ti ions appeared in the solution at a higher rate) at the point where the gold concentration was highest, however the open circuit potential increased, indicating that the sample was tending toward the passive region. It was also noted that the initial high potential, which corresponds to the presence of an oxygen layer, remained for a longer period of time before it dropped to the potential corresponding to pure, oxygen-free titanium. This extended time suggests that the oxygen layer was thicker or more dense on those samples which had been implanted with higher fluence of gold.

This investigation had two objectives: (1) to investigate the implanted ion profile of gold-implanted titanium using ion beam analysis techniques to determine if the oxygen on the surface of the sample is recoil-implanted and (2) to determine how these implanted oxides affect the return to passivity characteristics of titanium implanted with gold.

It is difficult to detect and quantify small amounts of low atomic mass impurities contained within a higher atomic mass substrate using Rutherford Backscattering Spectrometry because the yield from the substrate is so high that the small impurity signal cannot be distinguished [8]. In 1953, John Cameron identified five nuclear resonances for  $\text{He}^+$  scattered by oxygen, in the energy range

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from 2.4 to 4.0 MeV [9]. A very large cross section at 3.045 MeV makes it possible to detect very small concentrations of oxygen. The use of this narrow, well defined resonance has been used, mainly for accelerator calibration, but has also been experimentally demonstrated and applied in studies of oxygen depth profiles in  $\text{Si}_3\text{O}_x$  and  $\text{Mo}_3\text{O}_x$  by Hnatowicz et al. [10]. Nuclear resonant scattering (NRS) was used in this study to calibrate the accelerator and to improve the detection sensitivity for surface and recoil-implanted oxygen.

## 2. Experiment

Samples were cut from 99.7% pure titanium rods, and polished to a mirror finish. They were then mounted in a polymethyl methacrylate holder which only allowed the face of the sample to be exposed, and placed in a constant temperature (40°C), 20% sulfuric acid bath. The potential of the sample (working electrode) was monitored with respect to a saturated calomel electrode (SCE) and recorded. The passive layer of oxygen that forms spontaneously on the surface of titanium is known to be soluble in sulfuric acid, as is titanium itself. Since the open circuit potential of titanium oxide is different (more noble or less negative with respect to the SCE) from that of titanium, it is evident when the passive layer has dissolved, exposing pure titanium to the acid. A rapid drop in potential to approximately  $-0.7$  V, characteristic corrosion potential of pure titanium [11], occurred when the titanium entered the active corrosion region, indicating that the surface oxygen had been removed. This process will be referred to as acid cleaning.

Samples were then exposed in nitrogen, argon and a vacuum of  $10^{-6}$  Torr, and the acid test was repeated to ensure that the potential would immediately return to the value characteristic of pure, oxygen-free titanium. One sample (#1) was acid cleaned, exposed to air for two weeks allowing a stable layer of oxygen to form, and placed in the ion-beam target chamber (see Fig. 1). A second sample (#2) was acid cleaned and maintained in inert gas during immediate transfer to the same target chamber, and the chamber was evacuated. The vacuum was maintained better than  $1 \times 10^{-6}$  Torr in the target chamber throughout the pre-implant, implant and post-implant procedures.

The 1.7 MeV National Electrostatics 5SDH-2 Tandem Pelletron™ ion accelerator at Acadia Research Laboratory, was used to produce the  $^4\text{He}^+$  ions. All spectra were normalized to total charge striking the target but offset for the purposes of comparison in the figures. The first NRS spectra were obtained from samples #1 and #2 (Fig. 2) for pre-implant surface oxygen analysis using 3.05 MeV  $^4\text{He}^+$ . It is apparent from the figure that even with the precautions taken, either some oxygen remained on sample #2 or the storage environment was not entirely oxygen-

## Pelletron Accelerator System

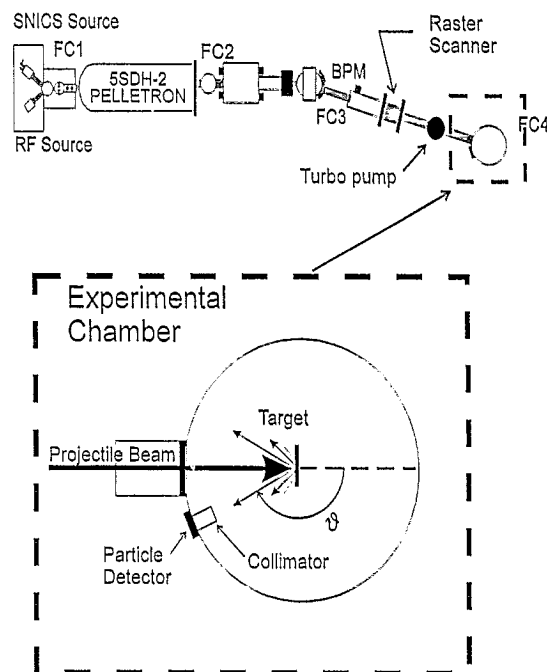


Fig. 1. Basic set-up of ion implantation and scattering experiments. The angle  $\theta$ , commonly referred to as the Rutherford scattering angle, was  $163^\circ$  in the target chamber used.

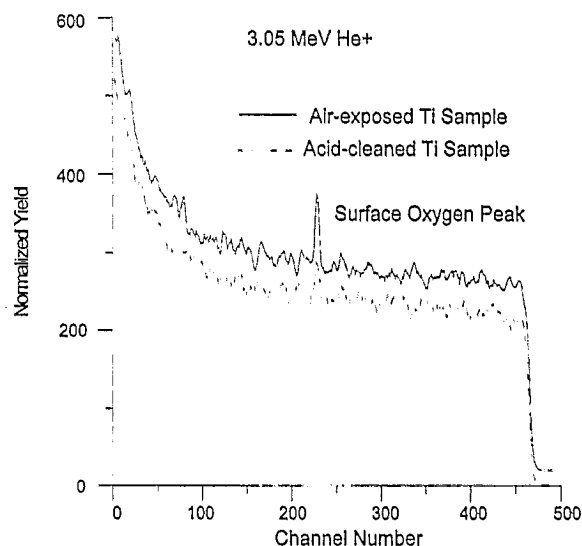


Fig. 2. Pre-implant 3.05 MeV  $^4\text{He}^+$  NRS spectra of air-exposed and acid-cleaned titanium test samples. A resonant oxygen peak is apparent in both spectra yet the air-exposed sample produced a relatively higher yield indicating that the oxygen was more dense. Spectra were normalized to ion charge collected and offset for comparison.

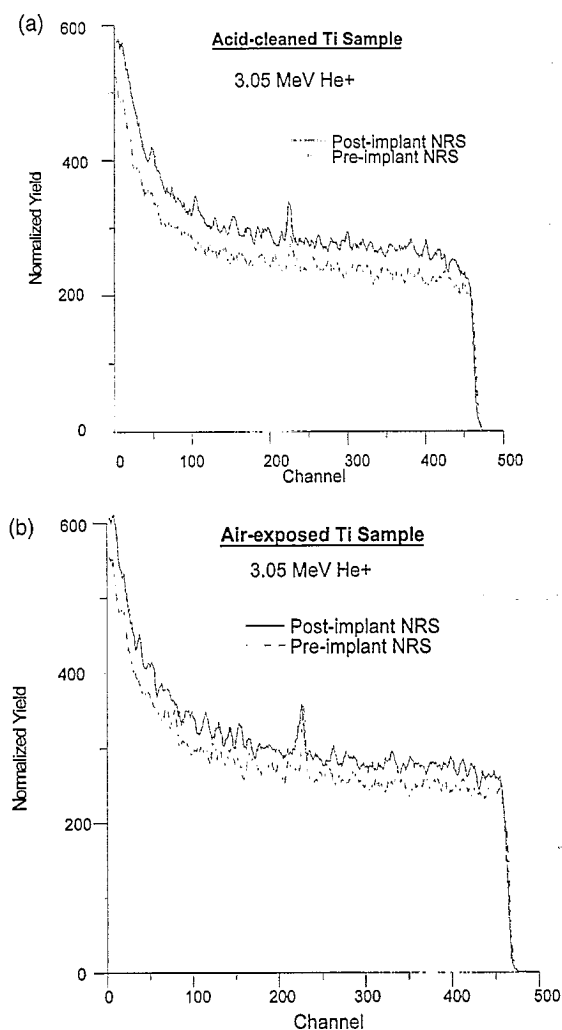


Fig. 3. 3.05 MeV He<sup>+</sup> NRS spectra of: (a) acid-cleaned and (b) air-exposed titanium samples. (a) Very little apparent difference in the pre-implant and the post-implant spectra indicates that the low density surface oxygen was not significantly affected by the gold ions; (b) a definite difference in both the width and relative height of the oxygen peaks, suggests that the dense oxygen layer was significantly affected by recoil collisions with the gold ions. Spectra were normalized to ion charge collected and offset for comparison.

free. A 1 MeV gold ion beam was rastered in the vertical and horizontal planes to ensure a uniform implant coverage and passed through a tantalum aperture which defined the implant area. Both samples were implanted with  $2 \times 10^{16}$  ions/cm<sup>2</sup> and post-implant NRS was performed to determine how the implantation of gold ions affected the surface oxygen layer. These spectra are compared to the pre-implant spectra in Fig. 3a and b. Standard (2 MeV) RBS spectra were also obtained to improve analysis of implanted gold ions (see Fig. 4) and illustrate the difficulty of detecting oxygen on titanium without the use of the resonance phenomenon.

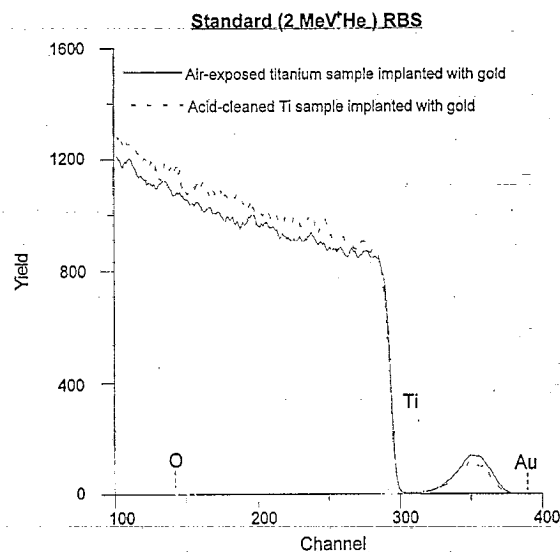


Fig. 4. Standard (2 MeV He<sup>+</sup>) RBS spectra of gold implanted titanium samples. This energy level improves analysis of the gold but does not make use of the oxygen scattering resonance. Spectra were normalized to ion charge collected and offset for comparison.

Samples #1 and #2 were then tested in sulfuric acid to determine how the presence of recoil-implanted oxygen affects the return to passivity characteristics of gold-implanted titanium as indicated by the open-circuit potential. Fresh acid was used in both cases and the results of these tests are shown in Fig. 5.

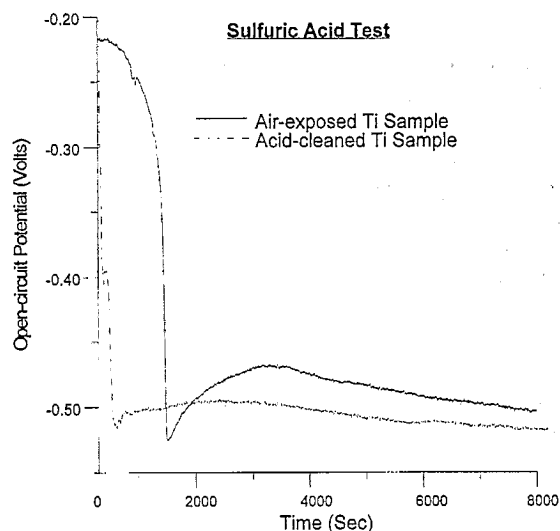


Fig. 5. Open-circuit potential curves measured with respect to a saturated calomel electrode in 20 wt.% sulfuric acid. Both samples were implanted with the same fluence of gold, but the one that contained more recoil-implanted oxygen approached a more noble potential.

A third sample (#3) was heated in an oven to 225°C for 15 h, after which the yellowish-gray oxide layer was visible. This was done to ensure that there was a high density of oxygen present so that the recoil-implanted oxygen could be detected more easily. In order to predict the maximum depth of oxygen and determine the  $\text{He}^+$  beam energies required to produce 3.05 MeV particles at that depth, it was assumed for simplicity that elastic collisions had occurred between the gold ions and the surface oxygen atoms. According to classical binary encounter theory [12] maximum energy transfer between two colliding particles occurs in a head-on collision. Therefore, a 1 MeV gold ion projectile colliding head-on with a stationary oxygen atom will result in a recoiling oxygen atom having an energy of 0.48 MeV. Using the TRIM code [13], the projected depth of 0.48 MeV oxygen in titanium is approximately 5470 Å. In order to produce a 3.05 MeV resonant scattering at that depth, a  $\text{He}^+$  ion beam of approximately 3.22 MeV is required, based on an average energy loss of 31 eV/Å.

This sample was implanted with the same fluence ( $2 \times 10^{16}$  ions/cm<sup>2</sup>) of gold, and NRS was performed at various incident beam energies around 3.22 MeV. A recognizable peak appeared in several of the spectra due to energy straggling of the incident beam [14] but was most pronounced at an incident energy of 3.208 MeV. NRS was then repeated at this energy on the acid-cleaned sample (#2) and on an unimplanted sample. These spectra are compared in Fig. 6.

### 3. Analysis of results

The ion beam analysis computer simulation program, RUMP [15], was used to determine the ion depth profiles from the various spectra. RUMP contains a subprogram called RES5 which provides the non-Rutherford resonance cross section data from Cameron [16] for analyzing NRS data. Note that some inaccuracies are introduced, due to energy straggling effects [17], when using this method to analyze buried ions. Analysis of pre-implant NRS spectra (Fig. 3a) indicate that, even in a controlled atmosphere, a thin layer of oxygen quickly formed on the surface of the cleaned titanium sample. However, because of the lower yield on the NRS spectra and the fact that the open circuit potential quickly dropped when controlled samples were placed in acid, it is evident that the concentration of oxygen remained low.

The surface oxygen peak in the post-implant NRS spectrum for the air-exposed sample is smaller yet broader than the pre-implant spectrum, indicating that the oxygen layer was less dense yet thicker as a result of the implantation (Fig. 3b). RUMP analysis revealed that the surface oxygen layer on the air-exposed sample (#1) was increased from 200 to 400 Å, whereas the layer on the acid-cleaned sample (#2) was not significantly affected by

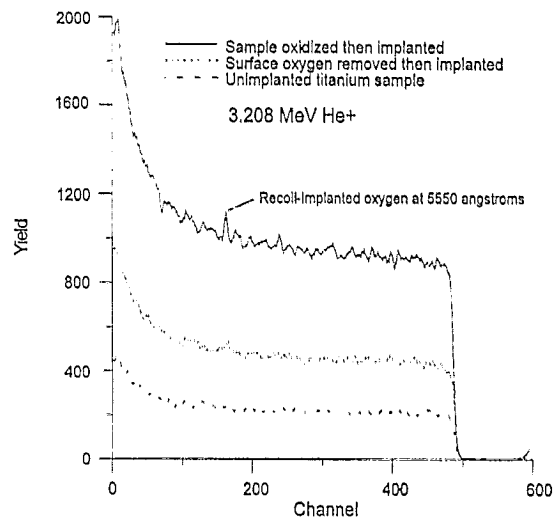


Fig. 6. 3.208 MeV  $\text{He}^+$  NRS spectra of three different titanium samples. One sample was oxidized before being implanted with 1 MeV gold ions. The energy loss factor caused the  $\text{He}^+$  ions to reach 3.05 MeV at the appropriate depth so that the scattering cross-section of the buried oxygen was large. Compared with the sample that was acid-cleaned and one that was not implanted, evidence of recoil-implanted oxygen is significant. Spectra were normalized to ion charge collected and offset for comparison.

the gold ions. The spreading of the oxygen layer on sample #1 can be seen in the oxygen profiles generated by RUMP as shown in Fig. 7. This thickening of the surface layer may account for the increased time required to remove the passive layer from implanted samples and is probably due

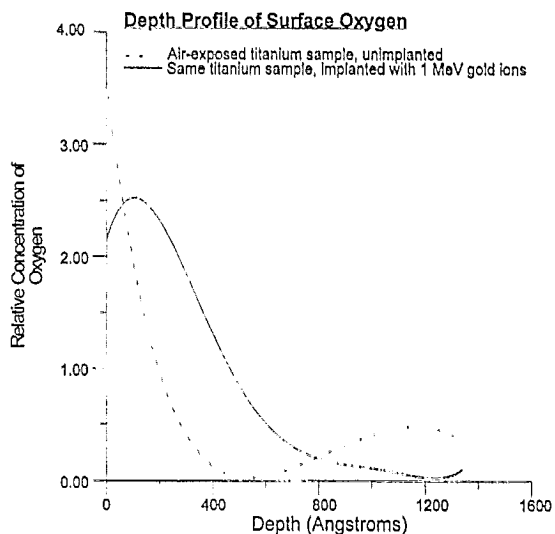


Fig. 7. Depth profiles of surface oxygen layer on the air-exposed titanium sample before and after being implanted with 1 MeV gold ions. These curves are polynomial fits of data generated by the RUMP PROFILE command, and illustrate that recoil collisions caused the oxygen layer to spread out and become less dense.

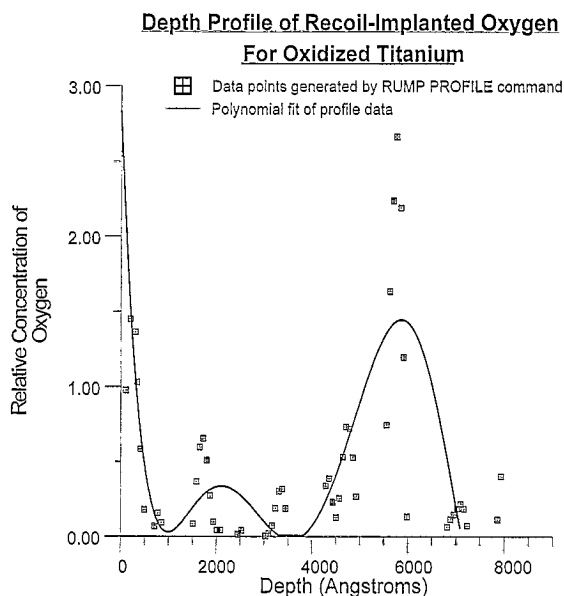


Fig. 8. Depth profile of recoil-implanted oxygen. This plot was generated from the 3.208 MeV spectral data in Fig. 6 using the PROFILE command in RUMP. The data from RUMP is shown and the curve is a polynomial fit to smooth the data.

to a large number of glancing collisions between the gold ions and oxygen atoms.

Examination of the deep recoil-implanted oxygen peak on the NRS spectrum (Fig. 6, solid line) shows that surface oxygen atoms are recoil-implanted into the titanium sample. Fig. 8 shows the oxygen profile data for the same sample generated by RUMP, and a polynomial fit to smooth the data. The large resonance corresponding to a depth of 5500 Å verifies the presence of recoil-implanted oxygen at that depth and appears to be highly concentrated in a region approximately 200 Å thick. However, any oxygen atoms located outside the narrow resonance region of the  $\text{He}^+$  ions do not contribute to the narrow resonance peak in the spectrum. This, along with the inaccuracies in the RUMP program already mentioned introduce uncertainties in the layer thickness. The 5500 Å depth determined by RUMP analysis is not significantly different from the 5470 Å predicted by the crude classical calculations. From the plot in Fig. 8, it is also apparent that some oxygen resides at a depth of about 2000 Å, which coincides with the maximum concentration of gold atoms. This may be due to lattice damage caused by the implanted gold or the increasing amount of gold at this depth may present a barrier to recoiling oxygen atoms resulting in a decreased range. The precise distribution of the recoil-implanted may not be well represented by the polynomial fit since it would be expected that the fraction of head-on collisions is relatively small, thereby producing a flat or decreasing oxygen recoil distribution as a function of depth. Further experiments are in progress to measure this distribution.

The implanted acid-cleaned sample (#2) exhibited no deep recoil implanted oxygen resonance peak. The lack of a noticeable peak was probably due to the presence of a relatively thin (200 Å) surface oxide layer from which oxygen could be scattered by gold ions (see Fig. 2).

#### 4. Conclusion

Ion implantation and ion beam analyses are excellent tools for studies in corrosion science, however it is already known that care must be taken when using RBS to analyze low  $Z$  impurities in high  $Z$  substrate materials. The large resonant scattering cross section of oxygen for 3.05 MeV  $\text{He}^+$  allows for the detection and analysis of oxygen in titanium both on the surface and buried beneath the surface. The results of this study show that the protective oxygen, which is responsible for the passive nature of titanium, is implanted into the substrate material along with the intended gold ions and has a measurable affect on the corrosion properties of the resulting alloy.

This *does not* imply that the spontaneous repassivation of titanium implanted with noble-metals seen in previous studies was caused by the presence of implanted oxygen. However, the presence of oxygen can introduce significant errors in test results if not included in the analysis. Also, since oxygen does not significantly affect the distribution of the implanted metal and because it is difficult to detect with standard RBS, other methods must be employed, such as NRS.

#### Acknowledgements

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